Chemistry 448
Problem Set 2

1.

$\epsilon_3 = 3\omega$

$\epsilon_2 = 2\omega$

$\epsilon_1 = \omega$

$\epsilon_0 = 0$

distinguishable particles
non-degenerate levels

For total energy $= 3\omega$ the only possible distributions are:

distribution	0	ω	2ω	3ω	No. of configurations	Probability
a	6	0	0	1	$\frac{7!}{6!\,1!} = 7$	7/84
b	5	1	1	0	$\frac{7!}{5!\,1!\,1!} = 42$	42/84
c	4	3	0	0	$\frac{7!}{4!\,3!} = 35$	35/84
					Total = 84	

Distribution b is MOST PROBABLE

Same levels, still distinguishable particles but degeneracies are $g_0 = 1$, $g_1 = 2$, $g_2 = 3$, $g_3 = 4$
Distributions are the same but the numbers of configurations for each distribution are different:

Distribution	no. of configurations	Probability
a	$\frac{7!}{6!\,1!}(1)^6 \cdot (4)^1 = 28$	28/560
b	$\frac{7!}{5!\,1!\,1!}(1)^5 \cdot (2)^1 \cdot (3)^1 = 252$	252/560
c	$\frac{7!}{4!\,3!}(1)^4 (2)^3 = 280$	280/560
	Total = 560	

Distribution c is most probable

2. Number of possible outcomes $= (8)^2 = 64$

sum= 2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
11	12	13	14	15	16	17	18	28	38	48	58	68	78	88
	21	31	41	51	61	71	81	82	83	84	85	86	87	
		22	23	24	25	26	27	37	47	57	67	77		
			32	42	52	62	72	73	74	75	76			
				33	34	35	36	46	56	66				
					43	53	63	64	65					
						44	45	55						

54

most probable is sum=9

Probability $= 8/64$

3. No. of ways in which the molecules can occupy the sites is

$$W = \frac{N!}{N_A!\, N_B!}$$

If $N_A = \frac{N}{2} = N_B$ $\qquad W = \dfrac{N!}{\left(\frac{N}{2}\right)!\left(\frac{N}{2}\right)!}$

Let $N! \simeq (2\pi N)^{1/2} N^N e^{-N}$

$$W_{Stir} \simeq \frac{(2\pi N)^{1/2} N^N e^{-N}}{\left[(\pi N)^{1/2}\left(\frac{N}{2}\right)^{\frac{N}{2}} e^{-\frac{N}{2}}\right]^2} = \frac{2^{1/2}\, 2^N}{(\pi N)^{1/2}}$$

For $N_A = N_B = 2$ $\qquad W = \dfrac{4!}{2!\,2!} = 6$ $\qquad W_{Stir} = \dfrac{2^{1/2} 2^4}{(\pi 4)^{1/2}} = 6.383$

discrepancy is 6.4%

more approximate form gives $W_{Stirl} \approx 2^N = 16$
very different from 6

For $N = 100$ $\quad W = \dfrac{100!}{50!\,50!} = 1.0089 \times 10^{29}$

$$W_{Stirl} = \frac{2^{1/2}\, 2^{100}}{(\pi 100)^{1/2}} = 1.0114 \times 10^{29}$$ quite good
only 0.25% error

More approximate form is

$$\ln N! \approx N \ln N - N$$

$$\ln 100! \approx 100\,(4.6052) - 100 = 360.52$$

$$\ln 50! \approx 50\,(3.912) - 50 = 145.6$$

$$\ln W \approx 69.32$$

$$W \approx 1.2744 \times 10^{30}$$ (worse but still not bad)

factor of 12.7 in error

4. Degeneracy of the four lowest energy levels
i.e. $J = 0, 1, 2, 3$

degeneracy is
electronic $(2S+1)(1 \text{ or } 2)$
vibrational 1
rotational $2J+1$
nuclear spin $I(2I+1)$ PARA
and $(I+1)(2I+1)$ ORTHO
or $(2I_A+1)(2I_B+1)$

	$J=0$	1	2	3
$H^{35}Cl$ $^1\Sigma$ $2S+1=1$ $(2\cdot\frac{1}{2}+1)(2\cdot\frac{3}{2}+1)=8$	8×1	8×3	8×5	8×7
$^{35}Cl_2$ $^1\Sigma_g^+$ fermions $J=$ even goes with $\frac{3}{2}(2\cdot\frac{3}{2}+1)=6$ para states $J=$ odd goes with $(\frac{3}{2}+1)(2\cdot\frac{3}{2}+1)=10$ ORTHO	6×1	10×3	6×5	10×7
$^{35}Cl\ ^{37}Cl$ $^1\Sigma^+$ $(2\cdot\frac{3}{2}+1)(2\cdot\frac{3}{2}+1)=16$	16×1	16×3	16×5	16×7
$^{14}N_2$ $^1\Sigma_g^+$ bosons $J=$ odd goes with $1(2\cdot1+1)=3$ para and $(1+1)(2\cdot1+1)=6$ ortho goes with $J=$ even	6×1	3×3	6×5	3×7
$^{15}N_2$ $^1\Sigma_g^+$ fermions $J=$ odd goes with $(\frac{1}{2}+1)(2\cdot\frac{1}{2}+1)=3$ ortho $J=$ even goes with $\frac{1}{2}(2\cdot\frac{1}{2}+1)=1$ para	1×1	3×3	1×5	3×7
$^7Li_2$ $^1\Sigma_g^+$ fermions just like $^{35}Cl_2$	6×1	10×3	6×5	10×7

	$J=0$	1	2	3
$^7Li_2$ $\;^1\Sigma_u^+$	10×1	6×3	10×5	6×7

because of

$J =$ odd goes with

$\frac{3}{2}(2 \cdot \frac{3}{2} + 1) = 6$ para states

$J =$ even goes with

$(\frac{3}{2} + 1)(2 \cdot \frac{3}{2} + 1) = 10$ ortho

$^{35}Cl_2^+$ $\;^2\Pi$	$4 \times 6 \times 1$	$4 \times 10 \times 3$	$4 \times 6 \times 5$	$4 \times 10 \times 7$

electronic $g = (2)(2) = 4$

fermions

$J =$ even goes with

6 para states

$J =$ odd goes with

10 ortho states